

Emission in the Deep Vacuum Ultraviolet from an Incandescently Driven Plasma in a Potassium Carbonate Cell

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Abstract

Electromagnetic radiation in both the visible and vacuum ultraviolet (VUV) spectral ranges was emitted from an incandescently driven plasma in a potassium carbonate cell after the potassium carbonate coated on a titanium mesh was heated to above 750°C in a hydrogen atmosphere. The pressure was between 0.1 and 1 mbar, and the hydrogen was dissociated by a hot tungsten wire. Bright visible light filled the annulus between the coaxial tungsten heater and the titanium mesh. This grid was at a floating potential. The emission of the H_α and H_β transitions as well as the L_α and L_β transitions were recorded and analyzed. In the latter spectral range, the spectra show rotational-vibrational transitions of molecular hydrogen which belong to the Werner-band-system of molecular hydrogen. The plasma generated in the incandescently driven cell has phenomenological similarities to that of low pressure electrical driven discharges such as striations of the plasma or the appearance of unipolar arcs ending on metal surfaces. However, the plasma seemed to be far from thermal equilibrium and dependent on the chemistry of atomic hydrogen with potassium. Details of the chemistry powering a novel VUV-light source could not be revealed within the frame of this contribution.

I. Introduction

Table top sources emitting radiation in the deep ultraviolet spectral range are gaining more and more interest in photochemistry due to the increased functionalization of surfaces, particularly in combination with lithographic processes [1]. The range and complexity of applications are wide and range from simple sterilization of large surfaces to sophisticated nano-patterning in production processes of microelectronics and biotechnology [2]. Well known sources such as electric sparks [3], capillary discharges [4], pseudosparks, hollow cathode discharges [5], laser sparks, and barrier discharges [6], to name a few, are suited for

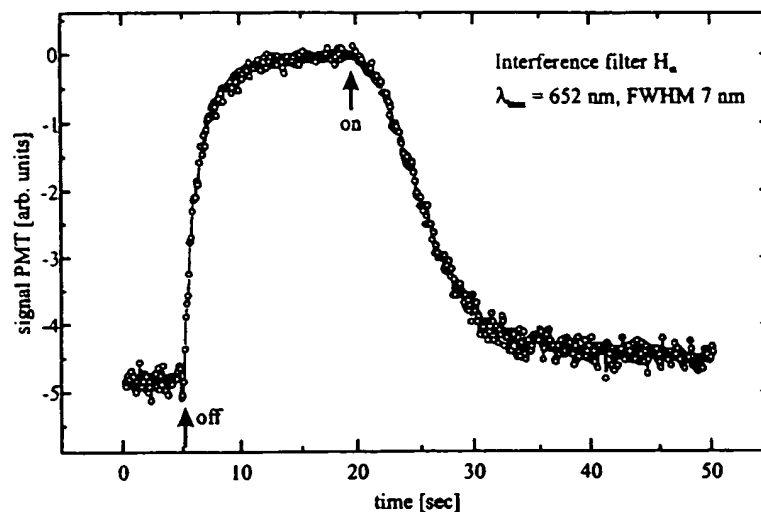


Figure 1: Emission of the cell as a function of time, while the heater current was turned off and on.

such photochemical work and are selected and developed further according to the specifications of the particular application.

Previously reported VUV emission of incandescently driven potassium carbonate cells in hydrogen [7] seemed to depend more on the chemistry of the potassium with hydrogen—with sodium carbonate no VUV emission was observed—and on the temperature of components in the cell than on a particular voltage or current applied to the cell. Figure 1 shows the decay and return of the H_α emission, which is indicative of an associated VUV emission, when the power was turned off and on in several ms. After turning off the heater power, the intensity dropped with a time constant of 2 seconds. With restoration of the original heater power, 10 seconds elapsed before the H_α emission reached its maximum again.

The following paper addresses the plasma and the VUV radiation generated in such a cell. The emission of the first two members of the Balmer and Lyman series were recorded with higher spectral resolution than before [7], and in contrast to earlier investigations, the tungsten wire was heated by external radiation as well as by ohmic heating.

II. Experimental set up

A. The Cell

Three different types of cells were used to investigate the formation of a low-voltage hydrogen plasma and the emitted radiation. One design, type I, was described previously [8]. In the second design, type II, the helical tungsten wire heater was replaced by two commercial 120 V halide bulbs connected in parallel. A tungsten wire was wrapped around the outside of the bulbs to serve as a hydrogen dissociator [9]. The tungsten wire in the type II cell as well as the titanium mesh were at a floating potential. All other components were the same as those of the type I cell. In the third design, type III, the thermal insulation of the quartz tube vacuum vessel of the type I cell was removed and replaced by an oven. An adjacent part of the tube had no insulation in order to allow for "side on" observation of the radiation. The rest of the quartz tube was covered by a brass tube that extended to the cap which provided the different supplies. The voltage supplied to the tungsten wire heater was increased step-wise from 20 V to 70 V. At 70 V, the color of the tungsten wire was similar to the one in the center of the oven.

For the Lyman series measurements, all of the cells were windowless and connected to a VUV spectrometer directly for "end-on" observation. The visible radiation was coupled to the spectrometer by glass fibers for "side-on" observation.

B. The Spectrometers

The light in the visible spectral range was analyzed by a grating spectrometer in Czerny-Turner mounting and recorded by a photomultiplier and oscilloscope as well as by an optical multichannel analyzer (OMA) system. A 1200 lines/mm grating blazed at 1000 nm was used. The light in the vacuum ultraviolet was analyzed by a scanning 1 meter grating spectrometer in Eagle mounting (McPherson, model 225) equipped with a grating of 1200 lines/mm blazed at 120 nm. The spectra were detected by a photomultiplier coated by a p-Terphenyl scintillator and recorded by an oscilloscope. The entrance and exit slits had a width of 50 μm . A pressure gradient was maintained between the cell and the pumped spectrometer.

III. Experimental Results

A. The Cell

The work was started with a type I cell. As soon as the temperature between the quartz wall and the thermal insulation of the cell exceeded 700°C , light was observed from the annulus between the helical tungsten heater and the titanium mesh coated with a thin film of potassium carbonate. The temperature outside of the quartz tube was increased to and held constant at 750°C . The bluish-white-colored emission that lasted for about one hour increased with temperature and was brighter than the glow of the tungsten heater. The experiment was repeated several times until the tungsten heater wire became brittle.

Rather than replace the tungsten wire, a series of experiments was performed next using the type II cell. With an electrically floating tungsten wire wrapped around the outside of the bulbs, the light in the annulus became bright after 10 minutes of heating and was observed to be different in color compared to the bright light emitted from the interior of the bulbs. The bluish-white light was easily observed by eye. The cell wall temperature was again 750°C . The light emission lasted about half an hour. Without the tungsten wire wrapped around the halide bulbs, no bluish-white light emission was observed.

No significant difference in the spectral emission or general performance could be determined between the type I and type II cells. Furthermore, the endurance of the bulbs in type II cell was not significantly better than that of the tungsten heater of the type I cell due to failure of the quartz walls of the bulbs under the resulting high-temperature conditions. The quartz of the bulbs developed plasticity with loss of mechanical stability above 1000°C . This behavior was not observed when the external tungsten wire was absent corresponding to the absence of the generation of the bluish-white light emission from the annulus. Since the operative temperature at the quartz wall of the type II cell was 750°C as well, it was concluded that an exothermic reaction was responsible for the generation of light in the annulus that also required the tungsten to be at a sufficiently high temperature and the presence of potassium carbonate on the titanium mesh.

Next a type III cell was studied. When a current was passed through the tungsten heater of a type III cell, a zone of about 5 – 10 windings was observed to have a significant lower temperature than the other windings as indicated by a difference in color. This cooler zone slowly migrated back and forth along the heater axis. Often several of these lower temperature

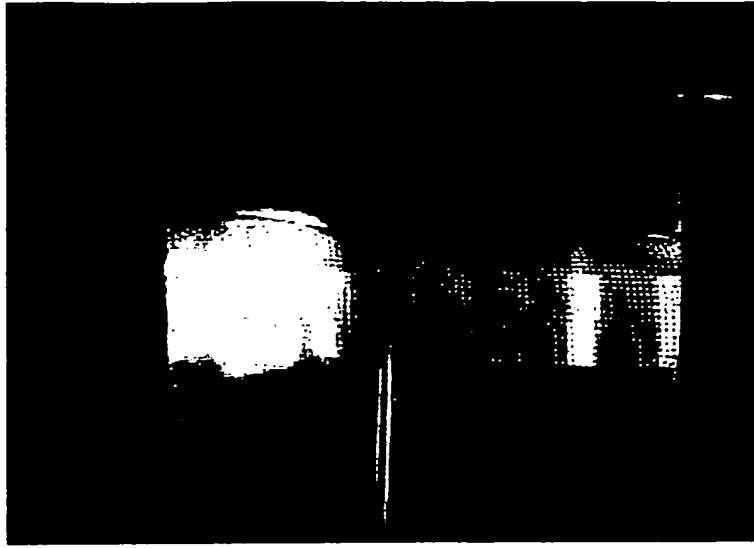


Figure 2: Photograph of the cell (type III). Bluish-white light can be seen at positions up to a few centimeters outside the oven (left) and the brass insulator.

zones were observed. A reasonable explanation for this phenomenon was that an electrical short formed across the zone of the darker windings due to a plasma created around the coil before the bluish emission in the annulus between the tungsten wire and the titanium grid could be visually observed. For the section of the heater that was observable, the voltage across the tungsten windings from one end of the cooler zone to the other was not more than 5 V. The emission of the tungsten wire and the associated voltage inside the insulating brass tube and the oven may have been different.

This segmentation of emission of the tungsten coil also remained active at a later stage when the light emission of the cell was fully developed as evident by the emission of the Balmer series of hydrogen. Then a greenish seam appeared around the dark zone directly pointing to an electrical short by a plasma. At this finally developed stage of the discharge, the bright zones of the tungsten wire shown in Figure 2 pointed to zones of higher axial electric fields. From the inhomogeneous light emission of the tungsten wire, it was concluded that an axial inhomogeneous field was generated in the annulus between the tungsten wire and the titanium mesh.

As shown in Figure 2, bluish light was emitted from the region between the titanium mesh and the quartz wall as well as from the annulus between the tungsten coil and the titanium mesh. A similar pattern was observed for the emission of white light. It was observed that a necessary

condition for this kind of emission was the existence of sufficient potassium carbonate on the titanium mesh, and the intensity of the bluish and white emission was related to the potassium carbonate concentration on the titanium mesh. In addition, it became evident that the temperature of the titanium mesh had to be sufficiently high to enable the emission. This was demonstrated by removing the oven and setting the tungsten coil at the rated voltage of 70 V for a time longer than that required to achieve strong emission. Only the red emission of the tungsten wire was observed. As soon as the oven was slipped over the quartz tube, the bluish and white emission started instantly.

Since the oven heating was sufficient to maintain the temperature of the titanium mesh sufficiently high for emission, the tungsten-coil heater power was reduced by decreasing its voltage. It was possible to sustain VUV light emission down to 20 V corresponding to about 0.2 V per winding and a field of about 0.1 V/cm. The light emission stopped with a voltage just below 20 V and returned at once when the voltage was restored to 20 V. When the voltage was set to zero for a while, the return of the light emission was delayed even when the voltage was quickly increased to 70 V. From these observations, it was concluded that the condition of a minimum tungsten-wire temperature was required in order to trigger the bluish and white light emission, when all of the other conditions were fulfilled. From the experiments with the light bulbs as heaters together with these findings, it was concluded that axial electric fields might be essential for the build up of the plasma and light emission, but an appropriately elevated temperature of the tungsten wire was necessary as well.

Radial plasma striations in the zones of bluish emission (see Figure 2) point to the existence of radial electric fields which might be generated due to chemical potentials in the vicinity of the titanium mesh or due to a Nernst potential because of a strong temperature gradient.

When the pressure in the quartz tube was raised to a couple of mbar, unipolar arcs developed on the titanium mesh. The dependence of this phenomenon on the voltage applied to the tungsten coil was similar to the case described above.

Striations of electric fields and their impact on electron properties in periodic states inside the plasma of a DC-glow-discharge have been analyzed in depth in references [10] and [11]. Since the observed space-resolved visible emission of the AC-driven cell is not very different from that in zones of DC glow discharges, it was concluded that the development of local electric field modulations and distinct non local electron properties may govern this kind of plasma as well. Dark zones in the annulus between tungsten coil and titanium mesh as well as outside the titanium mesh may have been zones of acceleration of free electrons. Electrons

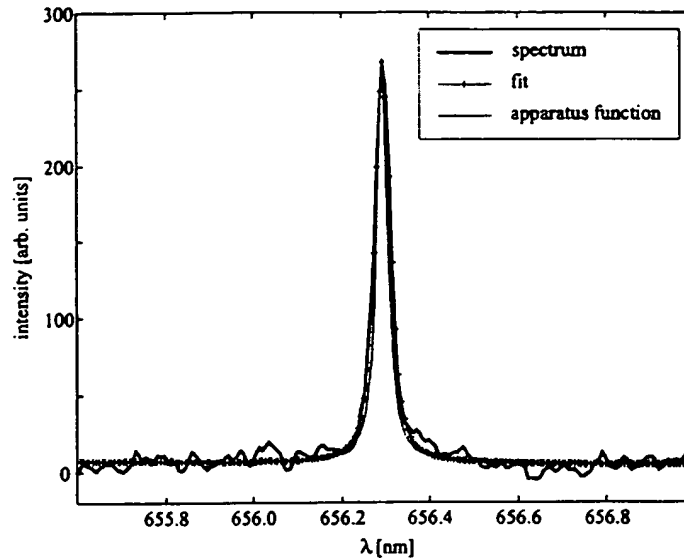


Figure 3: The emission of the H_α measured in second order together with its best fit and the apparatus function.

may have been accelerated axially and/or radially depending on the site in the cell. Inside the bright zones of the plasma the electrons may have lost a part of their energy due to interaction with heavy particles. A local pattern of the velocity distribution of the electrons in periodic states depends on partial pressures of the constituents and the local field distribution [10,11]. Both of these parameters could not be controlled during the reported experiments. It is therefore not too surprising, that the spectral emission such as that in the VUV varied between the different experimental runs as shown in Figures 4a and 4b. The plasma generated by the cell seems to be complex and requires further investigations. These issues are discussed in Sec. IV.

B. The Spectra

For the investigation in the visible spectral range, the wavelength was calibrated using a cold standard lamp that also served for the determination of the apparatus function which was fit by a Voigt profile of 0.96 pixels Gaussian and 3.89 pixels Lorentzian widths. In the first order, the width of the H_α transition ($\lambda = 656.28 \text{ nm}$) corresponds to that of the apparatus profile; whereas, in the second order, a broader and slightly asymmetric H_α profile was observed. Figure 3 shows the emission of the H_α transition measured in the second order with

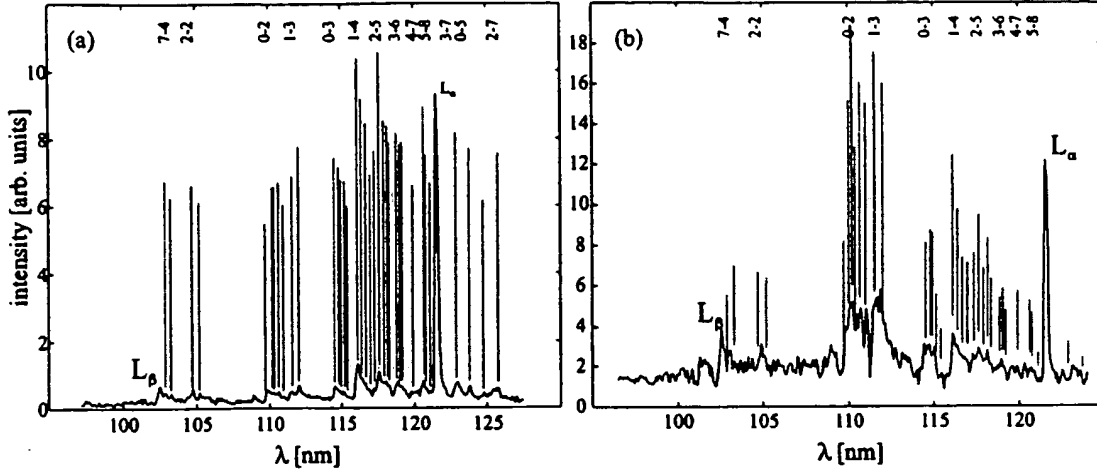


Figure 4: Examples of spectra of the L_α and L_β transitions showing rotational-vibrational transitions belonging to the Werner band system.

a reciprocal dispersion of 7.0 pm/channel together with a least squares fit. The calculated profile consists of three wavelength shifted Gaussian profiles according to the three fine structure transitions of H_α taking into account the intensity ratios given by [12]. The calculated profile is still asymmetric when it is convoluted with the measured apparatus function. Therefore, the asymmetry on the measured spectra can be attributed to the unresolved observation of the fine structure components. The fit gave a Gaussian width of (3.2 ± 0.9) pixels corresponding to (22 ± 0.06) pm. This served for an estimation of an upper limit of the ion temperature of $k_B T_e = (0.1 - 0.32) \text{ eV}$.

The H_β transition was identified in the spectra measured in first order. It was not observed in second order because of its low intensity. The intensity ratio of the H_α and H_β transitions was determined to be 15 ± 5 with a relatively high uncertainty due to the low intensity to noise ratio of the H_β transition. By assuming a Maxwell Boltzmann distribution of the level population, an electron temperature of $k_B T_e = (0.30 - 0.43) \text{ eV}$ was deduced. Since the electron density of the present plasma was small, the assumption of a Maxwell distribution was somewhat questionable. Nevertheless, only a slightly higher temperature of $k_B T_e = (0.32 - 0.48) \text{ eV}$ was found when a corona model was applied. In both cases, radiation transport was neglected in the calculations so that the temperature given represents an upper limit.

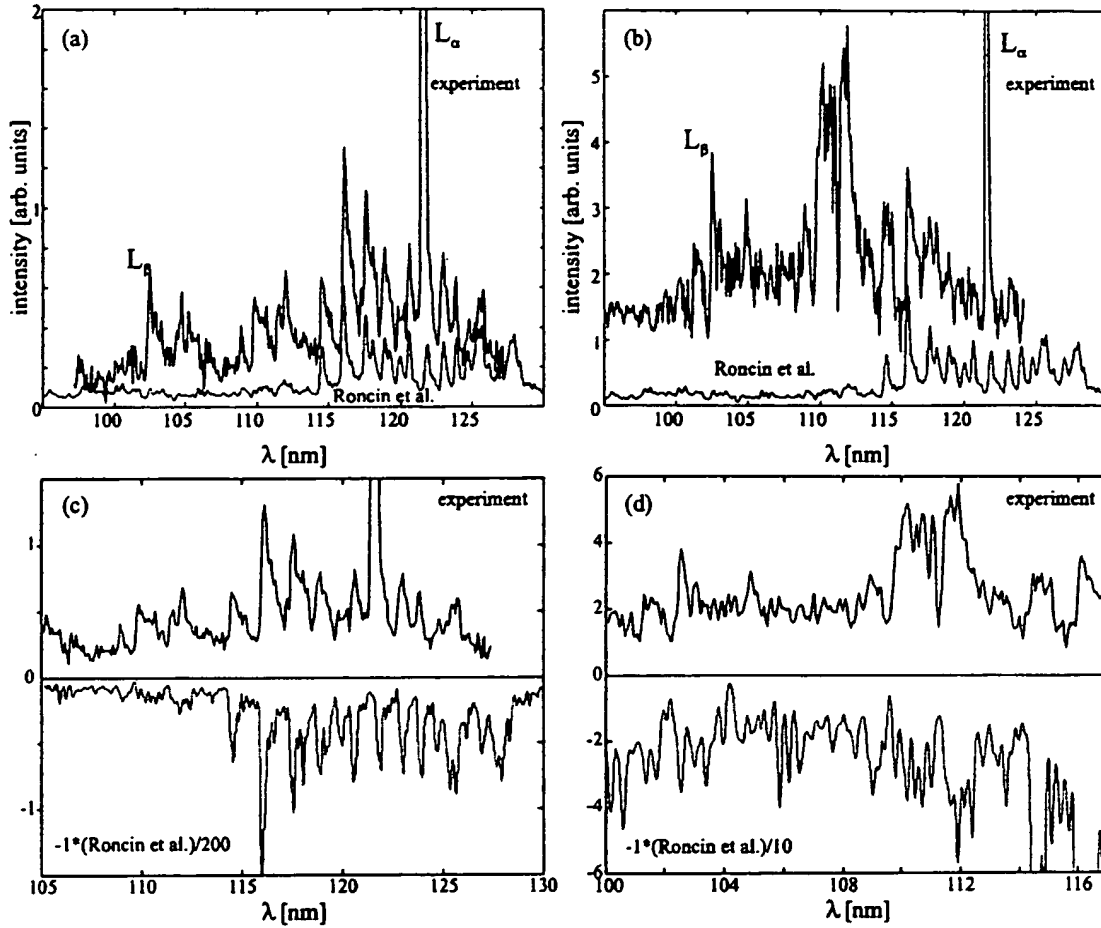


Figure 5: The measured spectra in comparison with a synthetic emission spectrum (intensity-scaled) of molecular hydrogen after [14]. a,c) and b,d) correspond to the experimental spectra in Figure 4a) and 4b), respectively.

Figure 4 shows two scanned spectra in the vacuum ultraviolet spectral range where the emission of the L_α and L_β can easily be seen. Strong emission of bands and lines were also observed in this wavelength region which will be discussed later. The intensity ratio of the L_α and L_β transitions was measured with a higher accuracy to be 16.5. For an optically thin plasma, the corresponding temperature of a Boltzmann level population is 62 eV. This excessive energy may indicate that this model is not applicable possibly because of the large distance of the energy levels. For these series transitions to the ground state, a corona model may be more suitable which gave an upper estimate of the electron temperature of

$k_B T_e = 1.6 \text{ eV}$. Nevertheless, this temperature was also factors higher than the above estimated temperatures indicating that at least the emission of the L_α may have suffered from radiation transport.

In summary, the data indicate that the electron temperature of the present plasma was not higher than $k_B T_e = 0.5 \text{ eV}$. On this basis, it was astonishing that the Lyman alpha and Lyman beta transitions appeared in the spectra since an excitation energy of 10.2 eV and 12.1 eV is required, respectively. The same holds for the Balmer series as well. The Lyman- α energy is a factor of about 20 above the measured thermal energy. The amount of electrons in the Maxwell tail that had enough energy to enhance the Lyman transition was 11 orders of magnitude lower than the total number of electrons.

Figure 5 shows the spectra of Figure 4 together with an emission spectrum of the Werner bands of the hydrogen molecules taken from reference [13]. The experimental spectra in this reference have a coincidence of 95% with theoretical results showing a high level of confidence. About 12,000 transitions were taken into account for the spectrum of Roncin et al. The relative intensities are presented as stated in reference [13], and the lines were convoluted with the measured apparatus profile. It is amazing to see the detailed similarity of the pattern of the energy levels between the experimental and the theoretical spectrum. Not only the vibrational but also numerous rotational transitions were identified in the spectrum of the cell. Similar to atomic emission, electronic transitions in low quantum numbers were preferred by the molecules in the plasma of the cell. However, the relative intensities of the spectrum in Figure 5(b) differed significantly from those of the spectrum of Roncin et al. in the range around 110 nm. This part of the spectrum belongs to a Werner band with $v' = 0$ and $v'' = 1$, respectively.

IV. Discussion

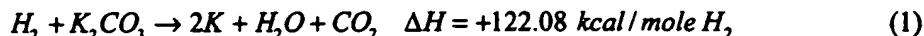
The emission of VUV radiation, and in particular, Lyman series and Werner band emission was observed from a low density plasma of quite moderate temperature similar to that in fluorescence tubes for general lighting. Such a plasma of an incandescently heated cell should not emit VUV radiation. The spectra showed that the plasma was far from thermal equilibrium. This was not too surprising because of the cell components, such as heater and titanium mesh etc., all may have contributed to a bimodal free-electron velocity distribution. But, the relevance of free electrons for the population of electronic levels is questionable

because of the preference for emission from a few specific electronic states of low quantum number. The same applies if a corona equilibrium was assumed.

Only blackbody radiation from the tungsten coil was observed at longer wavelengths. Based on the VUV emission, the plasma was predominately a hydrogen plasma. The ionization of atomic hydrogen requires 13.6 eV. In the cases where plasma was observed, no possible chemical reaction of the tungsten filament, the titanium screen, K_2CO_3 , and low pressure hydrogen at a cell temperature of 750°C could be found which accounted for the generation and sustaining of the plasma. In fact, no known chemical reaction releases enough energy to form an atomic hydrogen plasma as treated in the following discussion.

The enthalpy of formation ΔH_f of potassium hydride is -14.13 kcal/mole [14]. Thus, the formation of potassium hydride releases only 0.59 eV per atom. But, potassium hydride decomposes in this temperature range (288 to 415°C). Thus, it can not account for any emission of the hydrogen plasma.

The reduction of K_2CO_3 by hydrogen calculated from the heats of formation is very endothermic.



The reaction absorbs 2.5 eV per hydrogen atom.

The most energetic reaction possible with oxygen is the reaction of hydrogen to form water which releases 1.48 eV per atom of hydrogen; whereas, the energy of Lyman emission is greater than 10.2 eV per atom.

The dissociation of molecular hydrogen on the filament produces atomic hydrogen which may recombine to release 4.45 eV. Since atomic hydrogen is neutral, no contribution from the electric field of the filament is possible. Thus, excitation with energies of 4.45 eV or less is possible by the transport of thermal energy from the filament due to hydrogen dissociation followed by recombination. But this reaction is not sufficiently energetic to support the observed VUV emission.

Chemical energy may have been transported from regions outside of the annular region where most of the emission was observed. Dense and cold plasmas may have been created close to surfaces such as the titanium mesh due to chemical reactions. In such non ideal plasmas with electron densities close to solid density and temperatures below 0.5 eV, the potential energy of the electrons becomes comparable to their kinetic energy, and energy levels of bound electrons in atoms such as hydrogen are altered such that excitation and ionization energies are lowered [15]. This also applies to other elements of the plasma such as potassium. The electronic energy levels of the different species are further distorted when interacting with

each other. The dissociation of molecules and ionization of both the molecules and atoms may become more probable with more species. However, the lowering of the ionization and excitation energies by the state of "non ideality" in dense plasmas is only about 1 eV even for potassium. Thus, the most energetic chemical source possible, dissociated atomic hydrogen, could not have provided more energy than the Frank-Condon energy of 4.45 eV during recombination. Thus, this mechanism can not explain the hydrogen plasma.

The measured electron temperature, 0.5 eV, is over an order of magnitude too low to account for the hydrogen plasma. The filament electric field as the energy source of the excitation is also eliminated. The emission occurred even when the electric field was set and measured to be zero. The results can not be explained by electric field acceleration of charged species since the estimated external field of the incandescent heater is extremely weak, about 1 V/cm. The electron mean free path at the operating pressure range of 0.1 to 1 mbar is about 0.1 cm corresponding to a mean energy from the acceleration of electrons in the field of about 1 V/cm of under 1 eV. Thus, electron collisional excitation of Lyman emission or hydrogen ionization by a so called 'run-away-situation' of the velocities of free electrons is not probable. However, the observed plasma striations outside the titanium mesh close to the mesh points may have been due to local radial electric fields in the plasma not yet identified, where charged particles were accelerated in the dark zones to energies high enough to excite bound electrons in the brighter zones [11].

Temperature dependent electric fields also arise due to the greater mobility of electrons compared to ions. The generated voltage U for a plasma with a similar ion and electron temperature T is given by

$$U = \frac{kT}{2e} \ln \frac{m_i}{m_e} \quad (2)$$

where m_i is the mass of the ion such as the potassium ion or a proton, m_e is the electron mass, and e is the electron charge. From Eq. (2), the maximum voltage corresponding to the potassium ion is of the order of 1 V.

Multi-collisional processes may be possible [16], but very dense, high-pressure plasmas are required, and given an electron energy of 0.5 eV, about 30 concerted electron collisions would be required within 10^{-8} s—a definite impossibility.

Resonant energy transfer is possible to give predominantly Lyman α and Lyman β emission. Kurunczi, Shah, and Becker [17,18] observed intense emission of Lyman α and Lyman β radiation at 121.6 nm and 102.5 nm, respectively, from microhollow cathode discharges in high-pressure Ne (740 Torr) with the addition of a small amount of hydrogen (up

to 3 Torr). With essentially no molecular emission observed, Kurunczi et al. attributed the anomalous Lyman α emission to the near-resonant energy transfer between the Ne_2^* excimer and H_2 which leads to formation of $H(n=2)$ atoms, and attributed the Lyman β emission to the near-resonant energy transfer between excited Ne^* atoms (or vibrationally excited neon excimer molecules) and H_2 which leads to formation of $H(n=3)$ atoms. However, the formation of this plasma resulting in Ne_2^* excimers and excited Ne^* atoms required a field of over 10^4 V/cm; whereas, the field in the heated cells is on the order of 1 V/cm. Thus, this mechanism does not provide a source of energetic photons that may be resonantly transferred.

The titanium-mesh and the tungsten coil were present in all experiments. The emission was not observed with the cell alone, with hydrogen alone, or under identical conditions wherein Na_2CO_3 replaced K_2CO_3 . When the power was interrupted, the emission decayed in about two seconds. Decay was recorded over a time greater than 10,000 times the typical duration of a discharge plasma afterglow [19]. This experiment showed, that plasma emission was occurring even though the voltage between the heater wires was set to and measured to be zero for a time duration which was surprisingly extended. Since the thermal decay time of the filament for dissociation of molecular hydrogen to atomic hydrogen was similar to the plasma afterglow duration of the investigated source which requires the presence of K_2CO_3 , the emission was determined to be due to a reaction of K_2CO_3 with atomic hydrogen. The minimum temperature requirement of the tungsten wire for emission also demonstrated the emission reaction's dependence on atomic hydrogen.

A source of energy other than that provided by the electric field or known chemical reactions must be considered for explaining our experimental findings.

V. Conclusion

The generation of the Lyman and Balmer series and the Lyman Werner bands of molecular hydrogen requires energies significantly greater than 10 eV. The formation of a hydrogen plasma by the cell loaded with K_2CO_3 on titanium and operated in hydrogen required a minimum temperature. The heat from the filament and possibly the weak dipole field from the filament may sustain the hydrogen plasma; but, the latter is not essential because hydrogen lines were emitted during times when this voltage is set to zero. Furthermore, given the observations, free electrons can not excite these states. In the case that the free electrons should have been thermalized, their temperature was too low to contribute to excitation or ionization even from the tail of the velocity distribution. Longer range fields (of the order of mm) were

only about a 1 V/cm. In addition to electron collisional excitation, known chemical reactions, and resonant photon transfer, the lowering of the ionization and excitation energies by the state of "non ideality" in dense plasmas were also rejected as the source of ionization or excitation to form the hydrogen plasma.

The emission from a plasma was observed at low temperatures (e.g. $\approx 10^3$ K) from atomic hydrogen and potassium. The release of energy from hydrogen was evidenced by the hydrogen Lyman and Balmer emission which identified the presence of a hydrogen plasma. The persistence of emission following the removal of all of the power to the cell indicates that an unknown chemical power source is present. The implication is that a new plasma and light source for the vacuum ultraviolet has been discovered.

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